PB90-127986

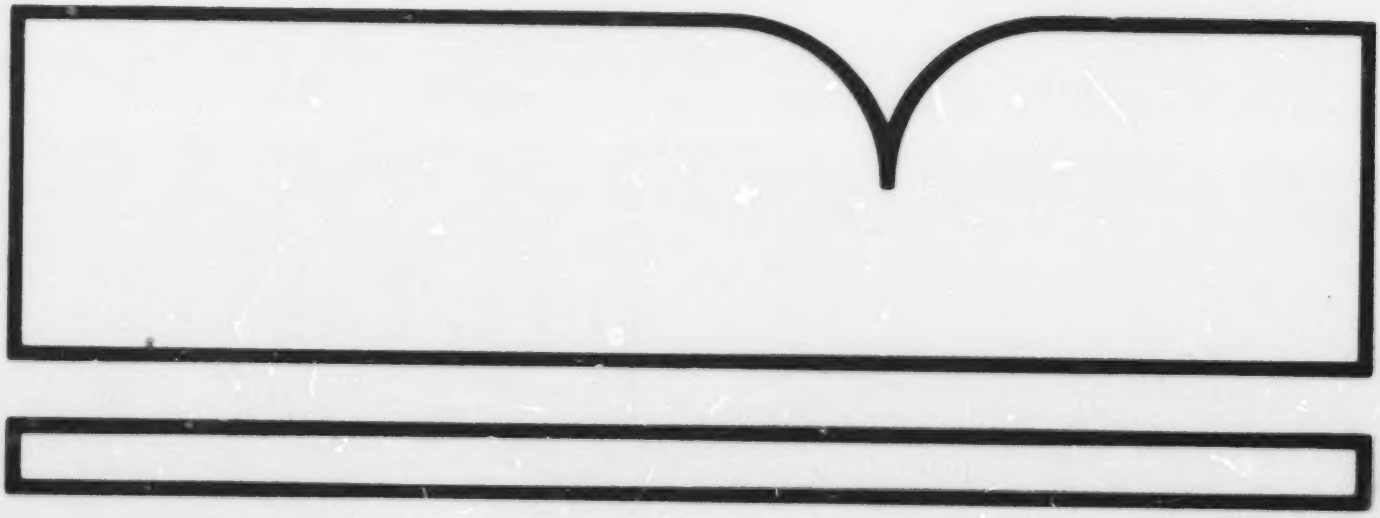
Solubility Studies Using a Generator Column for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin

Minnesota Univ.-Duluth

Prepared for:

Environmental Research Lab.-Duluth, MN

1989



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ERL-DUL-2387

1. REPORT NO.	2.	3.
EPA/600/J-89/157		PB90-127966

4. TITLE AND SUBTITLE
Solubility Studies Using a Generator Column for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin.

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Keith B. Lodge

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The Natural Resources Research Institute and Dept. of Chemistry, University of Minnesota, 3151 Miller Trunk Highway, Duluth, MN 55811

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
CR 813504

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Duluth, MN 55804

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA-600/03

15. SUPPLEMENTARY NOTES
Published in: Chemosphere 18(1-6):933-940 (1989).

16. ABSTRACT

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con't on pg 939

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to public	Unclassified	9
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

Chemosphere, Vol.18, Nos.1-6, pp 933-940, 1989
Printed in Great Britain

0045-6535/89 $3.00 + .00
Pergamon Press plc

EPA/600/J-89/157

SOLUBILITY STUDIES USING A GENERATOR COLUMN FOR 2,3,7,8-TETRACHLORODIBENZO-p-DIOXIN

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Abstract

The concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin in high purity water pumped through a generator column at 1ml/min is strongly dependent on temperature. Concentrations of dioxin observed are: 12.9 ± 1.2ppt at 4.3 ± 0.2°C and 483 ± 94ppt at 17.3 ± 0.1°C.

Introduction

Generator columns have been employed for solubility studies of hydrophobic organic compounds[1-4]. They essentially consist of a solid substrate coated with the compound of interest. The substrate is confined inside a tube through which purified water is passed. Flowrates are chosen to be sufficiently low so that the emerging water is at equilibrium with the coated substrate, i.e. the emerging water is saturated with the compound of interest so long as there is an excess of compound on the substrate. Substrates employed have included glass beads[2,3], Chromosorb W[4] and Florisil[1].

For polynuclear aromatic hydrocarbons, May & coworkers[2,3] studied the properties of generator columns in detail. They observed that stable saturated solutions were produced after passing an initial volume of water in the range of 100-500ml through the generator column. The concentration of compound in the resulting solution was independent of flowrate for rates between 0.1 and 5ml/min. By thermostating the columns, they were able to measure solubilities as a function of temperature.

Solubility studies have been reported for the common chlorinated hydrocarbons used as insecticides as well as for polychlorinated biphenyls[1]. Generator columns have found extensive application in bioassays[5]; they provide a convenient means by which to introduce hydrophobic compounds into water. In this context they have been termed "saturators"[5].

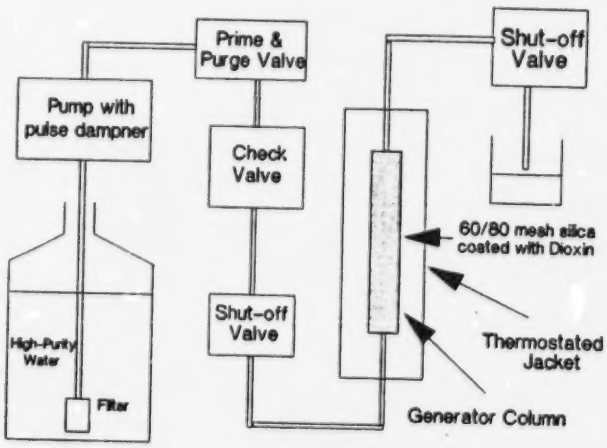
Recently, generator columns have been applied widely for research into the behavior of chlorinated dioxins in aquatic systems. The measurement of solubility has been reported for number of isomers[6-8] at environmentally significant temperatures. By employing solutions of humic materials, the interaction between dissolved matter and dioxins has been studied[9]. Also, they have proved valuable for dosing in bioassays[10]. Here the construction, application and properties of a generator column for 2,3,7,8-tetrachlorodibenzo-p-dioxin are described. This generator column was employed in a series of fish bioassays[11].

Experimental

Established techniques[2,3,7] have been followed closely in the construction of the generator column. An outline of the generator column and its pumping system are shown in Figure 1.

Figure 1.

Schematic Diagram of the Generator Column for 2,3,7,8-TCDD



Solvents. Water used to feed the generator column was Burdick & Jackson High Purity Water, which has been used in other solubility studies[12]. Solvent rinsing was performed using acetone followed by hexane then methylene chloride (all from Burdick & Jackson).

Column. The column, valves, fittings and tubing (0.02"ID, 1/16"OD) connecting the column to the shut-off valves were all standard HPLC components (Alltech) and were fabricated of 316 stainless steel. The column had an internal diameter of 4.6mm and was 250mm long. The fittings at each end contained a 2μ frit. The stainless steel tubing was cleaned using "Stainless Steel Kleen" (Alltech) followed by rinsing with hot water, acetone and hexane. Approximately 6g. of 60/80 mesh silica (sieved from 60/120 mesh material from Fisher Scientific) was used as the substrate. The silica was first solvent-rinsed before coating with dioxin. 100ug of 2,3,7,8-TCDD in nonane (Cambridge Isotope Labs) was placed in a 50ml recovery flask containing the silica. Using a rotary evaporator, the nonane was removed over a period of one hour; this operation was performed in a glove box along with the subsequent assembly of the generator column.

The assembled column was mounted in an HPLC water jacket (Alltech), which was fed by a 1:1 mixture of water and ethylene glycol pumped by a circulating water bath (Neslab Ex 500)

through a flow-through cooler (Neslab FTC 350A). Surface temperature probes (YSI series 400) were mounted under insulation on the inlet and outlet fittings of the water jacket. The temperature of the generator column was taken to be the mean of the inlet and outlet values. The shut-off valves at each end of the generator column serve to isolate it completely when necessary.

Pumping system. This was designed as a self-contained unit which could be detached from the generator column with ease. The high purity water was held in a 1l HPLC reservoir. The water was pumped out of the reservoir through a 2μ low pressure solvent filter using an FMI pump (model RHOCKC) in line with a pulse dampner. The wetted parts of the pump are a ceramic form of alumina and a fluorocarbon polymer. A bubble trap between the filter and the pump was found to be invaluable. The pumping system was primed using a syringe connected to the prime & purge valve. To prevent any possible contamination of the pumping system by accidental backflow from the generator column, a check valve is incorporated as the last unit of the pumping system. The individual components are connected by either stainless steel (1/16"OD) or teflon tubing (1/8" & 1/16"OD).

Extraction & Analysis. Aliquots of water were collected in 60ml separatory flasks directly from the generator column. They were then extracted and analysed by HRGC/HRMS using established techniques, which are thoroughly described elsewhere[13], and have been applied in a variety of studies[14-16]. However, since the sample is relatively "clean" in comparison to normal environmental samples, a simpler cleanup procedure was employed. After spiking the water with 500pg of $^{37}Cl_4$ 2,3,7,8-TCDD (internal standard), the water was extracted four times with 25ml of methylene chloride. The combined extracts were dried using sodium sulfate and reduced to about 0.5ml on a Kuderna Danish apparatus. The extract was then passed through a carbon column and eluted in the reverse direction with toluene. After reduction, the extract is spiked with 2ng of $^{13}C_{12}$ 1,2,3,4-TCDD (internal reference standard) prior to GC/MS analysis. This was performed using a 60m SP2330 GC column hooked to a Finnigan-Mat 8230. The signals from the internal standard (added before cleanup of the sample) and that from the internal reference standard (added just before GC/MS analysis) serve to define a response factor, from which may be calculated the recovery of the internal standard and thence the quantity of 2,3,7,8-TCDD in the sample. A "blank" water sample from the same source as that used to feed the generator column is analysed concurrently.

Solubility Studies at 4°C. One of the main purposes for constructing a generator column for 2,3,7,8-TCDD was to provide a supply of dioxin in water for a series of bioassays[11] involving Lake Trout (Salvelinus namaycush); the fish were to be held at 10°C. In order to avoid running water, saturated with dioxin at room temperature, through tubing at room temperature, it was considered judicious to saturate the water at a temperature well below ambient to avoid the propensity for dioxin to precipitate out under minor temperature fluctuations. The temperature of 4°C was chosen as a practical lower limit for our apparatus. It is asssumed that the solubility of dioxin increases with increasing temperature; this is observed for other isomers[7,8], and is supported by the data presented here.

Our studies to date have not included a full investigation of the generator column's properties with respect to flowrate. With other isomers, previous work[7] indicates that equilibrium is established at flowrates of 2.0 and 1.0ml/min; other studies[8] have used flowrates in this range. For convenience, a flowrate of about 1ml/min was chosen.

After passing approximately 300ml of high purity water through the column and exit tubing to "condition" it, subsequent aliquots of approximately 10, 15, 20 and 25 grams were collected in 60ml separatory flasks. The exact weight of solution collected was measured and then the solution was extracted immediately. A blank water sample of 900ml of the same high purity water feeding the generator column was extracted concurrently.

Solubility Studies at 17°C. Essentially the same procedure was followed except that the column temperature was controlled at 17°C. The ambient temperature was about 20°C so that the propensity for dioxin to precipitate out in the exit plumbing should be avoided. The column was conditioned with 450mls of the high purity water. Aliquots were then collected from the column and analysed as before.

Results and Discussion

We present the concentrations for each aliquot collected at 4°C and 17°C in Table 1.

Table 1. Concentration of 2,3,7,8-TCDD in Water passed through the Generator Column

at 4°C		at 17°C	
Mass of Solution (grams)	Concentration of dioxin (ppt)	Mass of Solution (grams)	Concentration of dioxin (ppt)
10.30	11.6	11.70	554
15.10	13.3	16.80	607
20.50	13.2	22.40	599
25.40	12.4	28.00	508
Column temperature was 4.3 ± 0.2°C. Flowrate was 1.13 ± 0.01ml/min. Column was conditioned with 300ml. Recovery of the internal standard ranged from 56-76%. Relative responses of the ions with mass-to-charge ratio 320 to those of 322 ranged from 0.76 to 0.79. Concentration of dioxin in the 900ml blank is estimated to less than 0.2ppt.		Column temperature was 17.3 ± 0.1°C. Flowrate was 1.13 ± 0.02ml/min. Column was conditioned with 450ml. Recovery of the internal standard ranged from 29-81%. Relative responses of the ions with mass-to-charge ratio 320 to those of 322 ranged from 0.77 to 0.79. Concentration of dioxin in the 50ml blank is estimated to be less than 0.1ppt.	

Solubilities should be independent of the sample size considered. We examine this idea by plotting the mass of dioxin in each sample against the mass of water and performing a linear regression analysis. Figures 2 & 3 show the plots along with the results of the linear regression analysis. In quoting the solubilities we use the slopes of the linear regression equations obtained by computing the intercept. That is, we measured the solubilities to be:

12.9 ± 1.2ppt at 4.3 ± 0.2°C 483 ± 94ppt at 17.3 ± 0.1°C

We see that the error in the solubility is larger at 17°C. In part this may be due to temperature effects; it is easier to control temperature further away from ambient. Here we observe a very strong temperature dependence; the solubility changes by a factor of 37 for a temperature of 13 degrees C! Effects in the exit tubing may be significant.

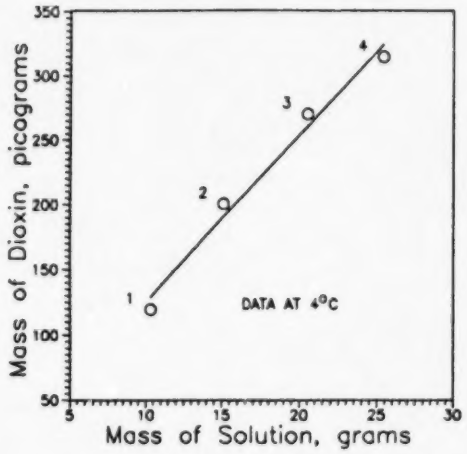


Figure 2.

Generator Column Data at 4°C

The mass of dioxin in each aliquot of solution is plotted against the mass of solution. The sequence of collection of each aliquot is represented by the data labels. Linear regression analysis yields the following:

Mass of dioxin (pg) = S_w.Mass of Water (g) + I

The line in the graph is plotted from this equation. The slope, S_w, represents the solubility. Here

$$S_w = 12.9 \pm 1.2 \text{ppt}$$

and the intercept, I = -4.1 ± 13.5pg.

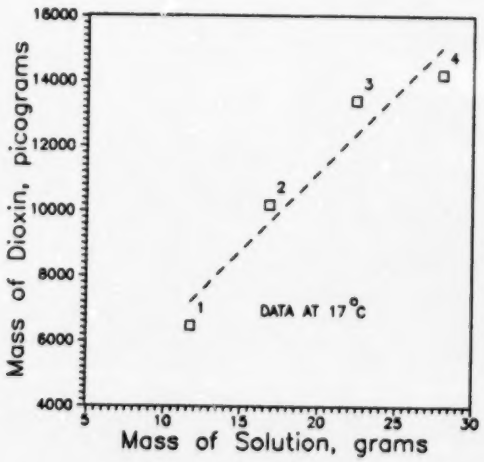


Figure 3.

Generator Column Data at 17°C

The mass of dioxin in each aliquot of solution is plotted against the mass of solution. The sequence of collection of each aliquot is represented by the data labels. Linear regression analysis yields the following:

Mass of dioxin (pg) = S_w.Mass of Water (g) + I

The line in the graph is plotted from this equation. The slope, S_w, represents the solubility. Here

$$S_w = 483 \pm 94 \text{ppt}$$

and the intercept, I = 1550 ± 1140pg.

How do the values determined here compare with those measured by other techniques? Other methods have given widely differing values. We compare the results of this method with other recent measurements[12,18] of 2,3,7,8-TCDD solubility in Table 2. Other results at ambient temperatures give values which are more in agreement with ours at 4°C than at 17°C! At present we do not have an explanation for this; one is needed if we are to be certain that the data obtained by any method truly represents the "solubility". We may ask whether there is a particular feature of the generator column method to account for this. This question may be partially addressed by looking at generator column data for other TCDD's.

Table 2. Recent Solubility Measurements of 2,3,7,8-TCDD Using Different Methods

Solubility ppt	Temperature °C	Remarks
12.9 ± 1.2	4.3 ± 0.2	generator column, this work
7.9 ± 2.7	20-22	method of Adams & Blaine (ref. 12)
12.5	22	^{14}C-thin film, Marple & coworkers (ref.18)
19.3	22	GC/LRMS-thin film, Marple & coworkers (ref.18)
483 ± 94	17.3 ± 0.1	generator column, this work

In Table 3, we compare solubilities of other TCDD isomers measured using generator column techniques[7,8]. We see that that the values for 1,3,6,8- & 1,2,3,7-TCDD at 20°C and 1,2,3,4-TCDD at 25°C are similar in magnitude to that for 2,3,7,8-TCDD at 17°C. This may be expected.

Table 3. Solubilities of TCDD's Measured By Generator Column Techniques

Temperature °C	Isomers 1,2,3,7-	1,2,3,4-	1,3,6,8-	2,3,7,8-
4		113 ± 7		12.9 ± 1.2
17				483 ± 94
20	430 ± 10		320 ± 20	
25		470 ± 21		
40	1270 ± 80	1170 ± 40	390 ± 40	

For 1,2,3,7- & 1,3,6,8-TCDD, the data is that of Friesen & coworkers (ref. 7).
For 1,2,3,4-TCDD the data is that of Doucette & Andren (ref. 8).
For 2,3,7,8-TCDD the data is from this work.

The octanol-water partition coefficients (K_{ow}) for certain tetra isomers have been measured by Burkhard & Kuehl[19]; $\log K_{ow}$ values are approximately 7. We may estimate the solubilities (S_w) from the following relationship[20]

$$\text{Log}S_w = -0.944\ \text{Log}K_{ow} - 0.01x(\text{melting point},^{\circ}\text{C}) + 0.323$$

where the units of S_w are moles per liter. For 162 aromatic hydrocarbons, Yalkowsky & coworkers[20] found that this relationship estimated solubility in the range 20 - 40°C within a factor of 3. For TCDD's, this yields solubilities with orders of magnitude in the 100ppt range. With higher values of K_{ow}, lower solubilities are predicted[18]. The value obtained by this method at 17°C is comparable to those obtained with other generator column methods applied to other tetra isomers; these all in turn are consistent with a model prediction.

However the unique feature in the data presented here is the very strong temperature dependence. This is emphasized by plotting the data in a Van't Hoff form[3,8] as is done in Figure 4. We see that there is a considerable difference in the enthalpies of solution.

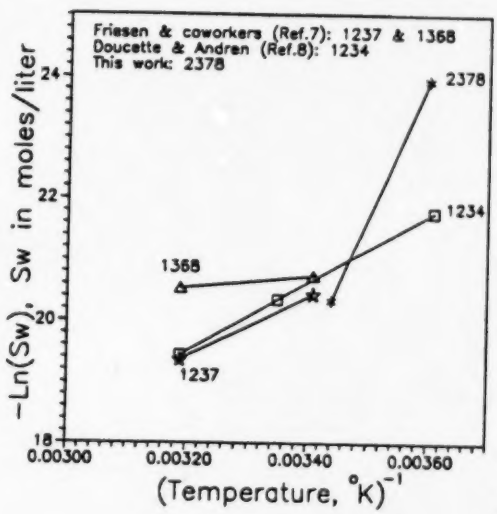


Figure 4. Temperature Dependence of Solubility for TCDD's

Here generator column data is plotted using the Van't Hoff Equation:

$$Ln(S_w) = -H_s/(RT) + \text{a constant}$$

where S_w is the solubility in moles/liter, H_s is the enthalpy of solution, kcal/mole, R is the gas constant and T is the absolute temperature, °K. The enthalpies of solution may estimated from the slopes of the lines; we obtain

for:		
	1,3,6,8-TCDD	2 kcal/mole
	1,2,3,7-TCDD	10 kcal/mole
	1,2,3,4-TCDD	11.2 kcal/mole
	2,3,7,8-TCDD	45 kcal/mole.

For only 1,2,3,4-TCDD are more than two data points available; the data shows excellent linearity. For the other isomers, linear behavior is assumed.

We have considerable confidence in our measurements at 4°C. The column operating at 4°C was employed to dose aquaria containing Lake Trout (Salvelinus namaycush)[11]. It was used in tandem with an injector system with seven ports. After a period of "conditioning", corresponding to the passage of about 1 liter of water through each port, we measured dioxin concentrations in 13 samples collected from the ports. Some samples were collected at the end of tubing which was of the order of 2-4 metres in length. The sample sizes ranged from 118.5g to 596.1g with a total sample size of 3.7Kg. Upon subjecting the data to linear regression analysis as described before we obtain:

Mass of dioxin (pg) = (15.3 ± 1.3) mass of solution (g) - (1037 ± 629pg).

This is in good agreement with the data obtained in the solubility study.

Conclusions

The concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin in high purity water pumped through a generator column at 1ml/min is strongly dependent on temperature. Concentrations of dioxin observed are: 12.9 ± 1.2ppt at 4.3 ± 0.2°C and 483 ± 94ppt at 17.3 ± 0.1°C. These data are consistent with those obtained from generator column techniques applied to other TCDD isomers[7,8]. However, they are not consistent with other recent solubility measurements[12,18] of 2,3,7,8-TCDD. It would be desirable to provide an explanation of these inconsistencies before it can said that the interaction of 2,3,7,8-TCDD with water is clearly understood. Should it prove to be the case that the data presented here can be truly identified as the solubilities, then this is of great environmental significance. Temperature dependence, since it is so strong, should be taken into consideration when modelling the distribution, transport and fate of 2,3,7,8-TCDD in the environment.

Acknowledgements

I am indebted to the following personnel of the Natural Resources Research Institute for sample extraction, analysis and general technical assistance; D.R. Marklund, S.W. Kohlbry, C. Harper and J. Libal. I am grateful to the following personnel in the U.S. EPA Environmental Research Laboratory at Duluth; P.M. Cook for stimulating discussions, B.C. Butterworth for HRGC/HRMS work, A.R. Batterman for logistical support and D. Lothenbach for bioassay assistance. The work described here was carried out under a Cooperative Agreement, CR-813504-01-0, with the U.S. EPA through its Environmental Research Laboratory in Duluth. In no way is it to be construed to represent the views of the EPA or its personnel.

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